REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*: 15-05-04

2. REPORT TYPE: Final Report

3. DATES COVERED: 01-06-00 to 30-04-01

4. TITLE AND SUBTITLE: The Molecular Basis of Humic Acid Reduction and its Role in Microbiologicallt Influenced Corrosion (MIC)

5a. CONTRACT NUMBER

5b. GRANT NUMBER: N00014-00-1-0775

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)

Florian Mansfeld

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Corrosion and Environmental Effects Laborartory (CEEL)
Department of Materials Science and Engineering
University of Southern California
Los Angeles, CA 90089-0241

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy St.
Arlington, VA 22217-5000

10. SPONSOR/MONITOR'S ACRONYM(S): ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AILABILITY STATEMENT

Distribution Unlimited

20040601 022

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Based on the experimental values of the corrosion potential and the polarization resistance it was demonstrated that iron respiration can protect steel from corrosion. A new electrochemical model that explains the mechanism of this process has been developed. This mechanism is based on the assumption that iron-reducing biofilms reduce the rates of both the oxygen reduction and the metal dissolution reactions that are involved in the corrosion of iron and mild steel.

15. SUBJECT TERMS

iron, biofilms, impedance spectroscopy, mineral dissolution, humic acid

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclass.	Unclass.	Unclass.	UP	3	Florian Mansfeld
					19b. TELEPHONE NUMBER (Include area code): (213) 740-3016

FINAL REPORT

GRANT #: N00014-00-1-0775

PRINCIPAL INVESTIGATOR: Florian Mansfeld

INSTITUTION: University of Southern California

GRANT TITLE: The Molecular Basis of Humic Acid Reduction and its Role in Microbiologically Influenced Corrosion (MIC)

AWARD PERIOD: 6 January 2000 - 3 April 2001

LONG-TERM GOALS: To determine how microbial biofilm communities affect the corrosion behavior of iron and mild steel.

OBJECTIVES: To identify the mechanisms of indirect mineral dissolution (mediated by microbial reduction of humic acid) and direct biofilm formation on minerals.

APPROACH: Transposon mutagenesis is used to make mutants in *Shewanella oneidensis* strain MR-1. Two separate genetic screens are performed: the first identifies mutants that are defective in their ability to reduce AQDS (a proxy for humic acid), the second identifies mutants that are defective in their ability to make biofilms on steel chips. Candidate mutants are subjected to a variety of tests to verify their phenotypes and further characterize their properties. The site of insertion of the transposon is determined. Depending on the nature of the mutation, individual mutants are studied further. Electrochemical impedance spectroscopy (EIS) has been used to compare the ability of selected mutants defective in either humic acid reduction or biofilm formation to influence the corrosion behavior of mild steel.

WORK COMPLETED: A system that allows to perform electrochemical impedance spectroscopy has been set up in Professor Newman's laboratory at Caltech. Software developed at CEEL/USC has been used to analyze impedance spectra and determine the changes in corrosion behavior due to the presence of selected mutants.

RESULTS: Based on the experimental values of the corrosion potential and the polarization resistance which is inversely proportional to the corrosion rate we have demonstrated that iron respiration can protect steel from corrosion, and we have developed a new electrochemical model that explains the mechanism of this process. This mechanism is based on the assumption that iron-reducing biofilms reduce the rates of both the oxygen reduction and the metal dissolution reactions that are involved in corrosion of iron and mild steel. We have published a paper on this discovery in Applied and Environmental Microbiology [1].

IMPACT/APPLICATIONS: Two important findings have come out of our work this past year. The first is that there appears to be a relationship between electron shuttling molecules and certain classes of antibiotics. The second is that we have shown that iron-reducing biofilms may protect iron and mild steel from corrosion. We believe that both of these findings will have a significant impact. The first, because it may change our thinking about the evolutionary basis for antibiotics; the second, because it may have practical consequences for how the concept of microbiologically influenced corrosion inhibition (MICI) will be used as an inexpensive, environmentally friendly method of corrosion protection.

TRANSITIONS: The results obtained in this project demonstrating that *S. oneidensis* strain MR-1 can protect steel from corrosion have influenced the research carried out at CEEL/USC dealing with MIC and its inhibition (MICI). We have begun working with two *Shewanella* strains to determine their effect on the corrosion behavior of a variety of materials such as an aluminum alloy, brass and mild steel exposed to artificial seawater.

RELATED PROJECTS: I have an on-going collaboration with a group at the University of Connecticut and a group at the University of California at Irvine which evaluates the concept of corrosion control using regenerative biofilms (CCURB) and is funded by the Electric Power Research Institute (EPRI). This project is currently in Phase III in which bacteria that have been shown in Phases I and II to inhibit corrosion of materials such as mild steel, stainless steel, brass and aluminum alloys are added to side streams in power plants for long-term monitoring of the corrosion behavior of these materials.

REFERENCES: [1] M. Dubiel, C. H. Hsu, C. C. Chien, F. Mansfeld and D. K. Newman, Appl. and Environ. Microbiology 68 (3), 1440 - 1445 (2004).

REFEREED PUBLICATIONS:

1. D. Örnek, A. Jayaraman,T. K. Wood, Z. Sun, C. H. Hsu and F. Mansfeld, "Pitting Corrosion Control Using Regenerative Biofilms (CCURB) on Aluminum 2024 in Artificial Seawater", Corros. Sci. 43, 2121 (2001).

2. A. Naguib and F. Mansfeld, "Evaluation of Microbiologically Influenced Corrosion Inhibition Using Electrochemical Noise Analysis", Corrosion Science 43, 2001 (2001).

3. A. Nagiub and F. Mansfeld, "Microbiologically Influenced Corrosion Inhibition (MICI) due to Bacterial Contamination", Materials and Corrosion 52, 817 (2001).

OTHER PUBLICATIONS (Conference presentations):

1. B. J. Little, R. I. Ray, P. A. Wagner, J. Jones-Meehan, C. C. Lee and F. Mansfeld, "Diagnosing Microbiologically Influenced Corrosion", Proc. 7th Int. Symp. on "Electrochemical Methods in Corrosion Research (EMCR'2000)", Budapest, Hungary, May 28 - June 1, 2000.

2. F. Mansfeld, "Evaluation of Microbiologically Influenced Corrosion (MIC) and its Inhibition with Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise Analysis (ENA)", Proc. ISMCC-2000 Int. Symp. on "Marine Corrosion and Control", Qingdao, Peoples Republic of China, July 30 - August 1, 2000, Ocean Press.

3. T.K. Wood, F. Mansfeld, D. Ornek, A. Jayaraman, Z. Sun, and C.H. Hsu, "Reduction in Pitting Corrosion Using Regenerative Biofilms on

Aluminum 2024 in Artificial Seawater", American Chem. Soc. National Meeting, San Francisco, March 2000.

4. B.C. Syrett, P.J. Arps, J.C. Earthman, F. Mansfeld, and T.K. Wood, "Corrosion Control Using Regenerative Biofilms (CCURB) - An Update", NACE Italia Conference on Corrosion in Refinery Petrochemical and Power Generation Plants, Venice, Italy, May 2000.

5. B. C. Syrett, T. K. Wood, F. Mansfeld, J. C. Earthman and P. J. Arps, "Corrosion Control Using Regenerative Biofilms (CCURB) - An Overview", paper No. 1272, Corrosion/2001, Houston,TX, March 2001 (NACE).

6. F. Mansfeld, C. H. Hsu, D. Ornek, T. K. Wood and B. C. Syrett, "Corrosion Control Using Regenerative Biofilms (CCURB) on Aluminum 2024 and Brass in Different Media", 198th Meeting, The Electrochem. Soc., Abstract No. 336, Phoenix, AZ, Oct. 2000, Proc. Symp. "New Trends in Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise Analysis (ENA)", The Electrochem. Soc., Vol. 2000-24, p. 99 (2001).

7. F. Mansfeld, "The Use of Electrochemical Techniques for the Investigation and Monitoring of Microbiologically Influenced Corrosion (MIC) and Corrosion Inhibition (MICI)", Int. Conf. "Biofouling and Materials", Frankfurt, Germany, June 2001.

8. A. Nagiub and F. Mansfeld, "Microbiologically Influenced Corrosion Inhibition (MICI) Caused by Bacterial Contamination", Int. Conf. "Biofouling and Materials", Frankfurt, Germany, June 2001.

9. F. Mansfeld, C. H. Hsu, D. Ornek, T. Wood and B. Syrett, "Corrosion Control Using Regenerative Biofilms (CCURB) on Al 2024 and C26000 Brass", paper No. 1270, Corrosion/2001, NACE, (2001).

10. F. Mansfeld, C. H. Hsu, D. Ornek, T. Wood and B. Syrett, "Ennoblement of Al 2024 and C26000 Brass in Different Media", paper No. 1258, Corrosion/2001, NACE, (2001).

11. D. Ornek, C. H. Hsu, F. Mansfeld and T. Wood, "Corrosion Reduction of Mild Steel 1010 and Aluminum 2024 by Phosphate-Secreting *Escherichia coli* Biofilms", ACS meeting, San Diego, CA, April 2001.